

POLY- AND METAPHOSPHATES

BY

ROBERT KEITH OSTERHELD

B.S., Polytechnic Institute of Brooklyn, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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POLY- AND METAPHOSPHATES

High temperature reactions constitute an important phase of the chemistry of phosphates. The phosphates resemble the molybdates, chromates, and vanadates with respect to the formation of isopolyacids. However, unlike these particular anions, it is necessary to make use of high temperature acid systems to form the condensed phosphates. In aqueous solution, only depolymerization takes place, the condensed phosphates ultimately being converted to orthophosphate. The use of high temperature bases, such as alkali metal halides, to effect these depolymerizations offers a possible approach to the preparation of a halophosphate.

EXPERIMENTAL

Considerable use was made of the technique of differential thermal analysis in these investigations. A small muffle type electric furnace was used for heating the samples. Sample temperatures were recorded continuously by means of an automatic recorder. The differential in temperature between the sample and a similar amount of ignited aluminum oxide was recorded simultaneously on a second recorder. The temperature sensing units for both these purposes were Pt-90Pt10Rh thermocouples. The thermocouple and recorder combination used to determine the sample temperature was calibrated periodically. For those cases in which heating curve data were required, the heating rate was controlled to eight to ten degrees per minute. This was accomplished through the use of a controller to maintain a constant differential between the furnace muffle and the aluminum oxide sample.

A. The System Sodium Fluoride-Sodium Metaphosphate

The system potassium fluoride-metaphosphate had been studied by Amadori (1). The data for the system reveal the existence of two compounds: the monofluophosphate, $\text{KF} \cdot \text{KPO}_3$ or $\text{K}_2\text{PO}_3\text{F}$, which possesses a congruent melting

point; and $2\text{KF} \cdot \text{KPO}_3$, which melts incongruently. Sodium monofluophosphate has been shown to form when sodium fluoride and sodium metaphosphate are fused briefly (3). The thermal stability characteristics of this material were not determined. For this reason, and to contrast the weaker base, sodium fluoride, with the potassium compound, the system sodium fluoride-metaphosphate was investigated from 0 to 60% NaPO_3 . Melts richer in sodium metaphosphate would not crystallize reproducibly upon cooling; the melt at 80% NaPO_3 cooled to a glass.

The phase diagram constructed from cooling curve data shows that two compounds form in this system. The monofluophosphate melts incongruently at 566° and undergoes solid-phase transitions at 406° and 357° . A second compound, $2\text{NaF} \cdot \text{NaPO}_3$, melts congruently at 655° . Cooling curves near the 2:1 composition show a strong break at 566° , corresponding to the formation of monofluophosphate. Consequently, the 2:1 compound must be considered unstable with respect to sodium fluoride and monofluophosphate below 566° . Although analogous compounds form in the sodium and potassium systems, it is interesting that the thermal stability characteristics are reversed. Sodium fluoride and the compound $2\text{NaF} \cdot \text{NaPO}_3$ form an eutectic mixture at 15.8% NaPO_3 (nominal) and melting at 615° . The eutectic composition corresponds to a mixture of 23.1% ($2\text{NaF} \cdot \text{NaPO}_3$) and 76.9% NaF . A second eutectic, between $\text{Na}_2\text{PO}_3\text{F}$ and NaPO_3 , exists in the area richer than 60% in metaphosphate. Its position could not be determined by the use of cooling curves since the high metaphosphate content inhibited crystallization.

B. The Systems Sodium Chloride-Sodium Metaphosphate and Potassium Chloride-Potassium Metaphosphate

Although the chloride ion would be expected to be a weaker base than fluoride, there was a possibility that alkali metal chlorides might serve to depolymerize the corresponding metaphosphates and produce chlorophosphates. The sodium chloride-metaphosphate system was investigated sufficiently

to demonstrate that no chlorophosphate is obtained. The corresponding potassium compounds had been reported previously to form only an eutectic (2). This earlier work was verified.

C. The System Potassium Pyrophosphate-Potassium Metaphosphate

Although previously reported data (4) for the system potassium pyrophosphate-metaphosphate showed no compounds to form between these components, it seemed likely that potassium triphosphate should be produced and possible that potassium tetrphosphate might exist. Samples for this investigation were prepared by heating appropriate mixtures of potassium dihydrogen and monohydrogen orthophosphate at 575°. Thermal analyses and chemical analyses of samples thus prepared proved that potassium triphosphate does form as a compound melting incongruently at 650°. It forms an eutectic with potassium metaphosphate at 74.3% KPO_3 (nominal). The eutectic melts at 620° and corresponds in composition to actual mixture containing 34.6% $\text{K}_5\text{P}_3\text{O}_{10}$ -65.4% KPO_3 . Potassium tetrphosphate does not exist in samples prepared at 575°.

D. Mechanism of the Potassium Dihydrogen-Monohydrogen Orthophosphate Reaction

The use of the reaction between potassium dihydrogen and monohydrogen orthophosphate to prepare the samples for the pyrophosphate-metaphosphate system led to consideration of the mechanisms 1) by which the reactants form triphosphate and 2) by which the individual reactants undergo dehydration.

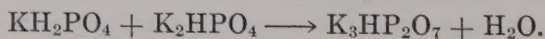
Thermal analysis of potassium dihydrogen orthophosphate showed that the rate of dehydration becomes appreciable at 208°. A strong endothermic process takes place at 258°. Since it is possible to prepare disodium dihydrogen pyrophosphate by partial dehydration of sodium dihydrogen orthophosphate at 210°, an attempt was made to prepare potassium

dihydrogen pyrophosphate at several temperatures between 208° and 258°. In each case water was lost smoothly until complete dehydration to metaphosphate had occurred. Metaphosphate formed early in the reaction and at no time was there present any appreciable amount of pyrophosphate or of any other intermediate. This indicated that potassium dihydrogen pyrophosphate is too unstable thermally to be isolated in such a reaction. Thermal analysis of the compound obtained in another way proved that its dehydration commenced below 200° and became rapid at 232°.

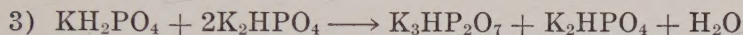
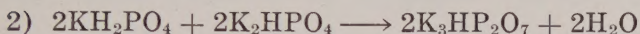
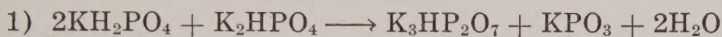
The heating curve for potassium monohydrogen orthophosphate demonstrated that the conversion into pyrophosphate proceeds in two steps: the first from 282° to 332°, and the second between 400° and 462°. Samples heated at 325° lose one-half of their constitutional water. The second half can be removed by heating to 460°. Chemical and x-ray analyses indicate the intermediate material to be a mixture of potassium monohydrogen orthophosphate and potassium pyrophosphate in the mole ratio 2:1.

Thermal analyses of samples containing 2:1, 2:2, 3/2:2, and 1:2 mole ratios of potassium dihydrogen to monohydrogen orthophosphate indicated that in each case a reaction started around 180-200° and became steady in the region between 230° and 250°. Comparison with the heating curves for the pure reactants made it clear that this reaction is not due to either component acting as an individual.

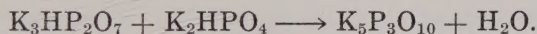
A temperature of 245° was chosen as one which would be likely to bring this initial reaction to completion. Samples containing 2:1, 2:2, and 1:2 mole ratios of potassium dihydrogen to monohydrogen orthophosphate were heated to constant weight at 245°. A comparison of weight loss data and analyses of the products with the results predicted by the various possible reactions indicates that the major reaction at this temperature is:



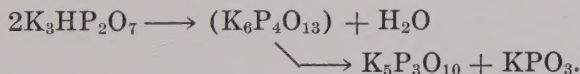
Strong evidence for this is the fact that the x-ray diffraction pattern of the 2:2 mole ratio product does not contain the strong lines of any of the common potassium phosphates. For the three mole ratios investigated here, the complete reactions at 245° are:



The mixtures in equations 2) and 3) are of particular interest, 2) because it involves a new compound and 3) because upon heating to a sufficiently high temperature it forms potassium triphosphate. The constant weight products at 245° of equations 2) and 3) were subjected to thermal analysis to determine their behavior at higher temperatures. The major reaction in the $\text{K}_3\text{HP}_2\text{O}_7$ - K_2HPO_4 mixture produced by equation 3) was found to start at about 255°. Samples heated to constant weight at 325° were found to have been essentially completely converted to triphosphate. This reaction may be represented by the equation:



Thermal analysis shows that further reaction of $\text{K}_3\text{HP}_2\text{O}_7$, obtained as the product of the process represented by equation 2), takes place at a somewhat higher temperature. Heating to constant weight at 325° will complete the reaction, however. The product was found by analysis to contain 24.0% and 75.6% of its P_2O_5 content as metaphosphate and triphosphate, respectively. It may be postulated that an unstable tetraphosphate intermediate forms and subsequently disproportionates in accordance with the following equation:



BIBLIOGRAPHY

1. Amadori, M., Atti reale acad. Lincei *21 II*, 183 (1912).
2. Amadori, M., *ibid*, *21 II*, 688 (1912).
3. Hill, O. F., Ph. D. Thesis, University of Illinois, 1948.
4. Parravano, N., and Calcagni, G., Z. anorg Chem. *65*, 1 (1910).

VITA

The author was born April 19, 1925 in Brooklyn, New York. Since that time he has resided in Rockville Centre, New York, attending the public schools of the neighboring Oceanside until his graduation from high school in June, 1942. In the fall of that year he entered the Polytechnic Institute of Brooklyn as the holder of a Nichols Scholarship. During his upper three years at Brooklyn Polytechnic he was employed on a government sponsored research program. He received the degree of Bachelor of Science in Chemistry in June, 1945.

The period from September, 1945 through January, 1947 he spent in the United States Air Force as an airway traffic controller and control tower operator in the Army Airways Communications System, reaching the rank of sergeant. During the last half of 1946 he was chief controller and NCOIC of the Manila Airway Traffic Service (Phillippine Islands).

The spring semester of 1947 he spent at the Polytechnic Institute of Brooklyn as a quarter-time teaching assistant and half-time research assistant. In Septem-

ber of 1947 he entered the Graduate College of the University of Illinois. He served as a teaching assistant in the Department of Chemistry from September, 1947 to June, 1948. In September, 1948 he was awarded the Victor Chemical Works Fellowship, which he has held since that time.

The author is a member of the American Chemical Society, the American Institute of Chemists, Sigma Xi, and Phi Lambda Upsilon.

He is a joint author of the following papers:

1. "Function of Fluxes in the Preparation of Infrared Sensitive Phosphors of the Alkaline Earth Sulfides and Selenides," Primak, Osterheld, and Ward, *J. Am. Chem. Soc.* *69*, 1283 (1947).
2. "Preparation of Some Infrared Sensitive Phosphors," Ward, Osterheld, and Rosenstein, *Inorganic Syntheses*, Vol. 3. In press.
3. "Hetero- and Isopolyacids," Audrieth and Osterheld, *Encyclopedia of Chemical Technology*, Vol. 6. In press.

